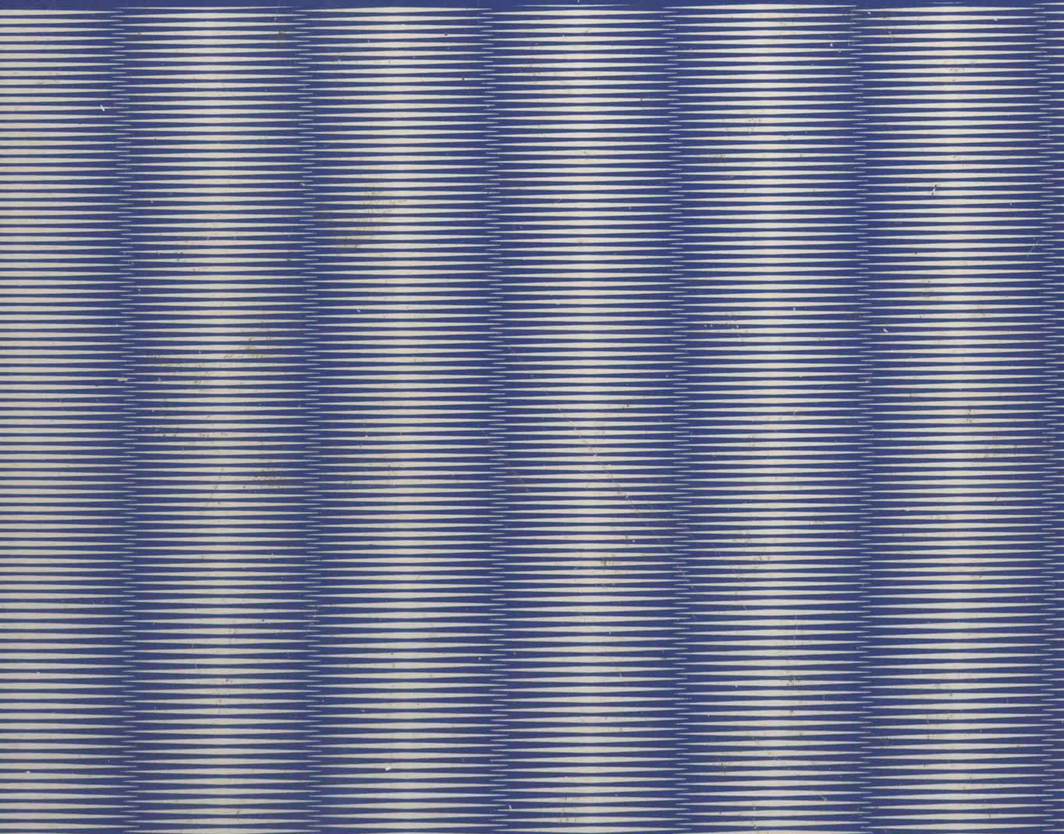
Field, Thermionic, and Secondary Electron Emission Spectroscopy

A. Modinos



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To Penny and Evris

PREFACE

Apart from their well-known technological applications, field, thermionic, and secondary electron emission can be and are often used as spectroscopies, i.e., as a means of investigating the electronic properties of the emitting surface. It is the aim of this book to present the theory of field, thermionic, and secondary electron emission spectroscopies from a unifying point of view and to demonstrate the applicability of the theory to the analysis of electron emission data from individual surfaces. The book is reasonably self-contained, although certain sections require some knowledge of the quantum theory of scattering, and may serve as an introduction to the subject. At the same time it presents a report on recent advances which will be of interest to the specialist.

The traditional theory of field and thermionic emission, based on the free-electron model for metals, its applications, and its limitations, are discussed in Chapters 1 and 2. Those aspects of the theory of solids and their surfaces which are necessary for a quantitative theory of field, thermionic, and secondary electron emission spectroscopies are discussed in Chapters 3 and 4. The theory of these spectroscopies and discussion of relevant experimental data takes up the remaining six chapters of the book.

It is assumed, unless otherwise explicitly stated, that the emitting surface is a single-crystal plane. In the case of field emission from adsorbate-covered metal surfaces (Chapter 6) or field emission through singly adsorbed atoms (Chapter 7) it is assumed that the substrate surface is a single-crystal plane of the metal under consideration. It is also assumed that the emitted current density is sufficiently small, so that the space charge in front of the emitting surface is negligible.

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CHAPTER ONE

ELECTRON EMISSION FROM FREE-ELECTRON METALS

1.1. THE FREE-ELECTRON THEORY OF METALS

The free-electron theory of metals proposed by Sommerfeld (1928) has provided the basis for practically all quantum-mechanical theories of electron emission from metals until relatively recently, and some important formulas derived on the basis of this theory are still extensively used in the analysis of relevant experimental data. It is, therefore, appropriate to begin our present study with a brief exposition of the free-electron theory of these phenomena. At the same time we shall point out the limitations of this theory which have become evident by the accumulation of experimental data which it cannot explain.

The free-electron theory of metals is based on the assumption that the conduction band electrons behave, effectively and for many practical purposes, as if they were free particles. In this model the electron states (in the conduction band) are described by plane waves

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{L^{3/2}} \exp\,(i\mathbf{k} \cdot \mathbf{r}) \tag{1.1}$$

where $L^3 \equiv V$ is the volume of the metal, which is assumed to be very large, and $\mathbf{k}$ (the wave vector) is given by

$$\mathbf{k} = \frac{2\pi}{L}\,(n_x,n_y,n_z) \tag{1.2}$$

where n_x,n_y,n_z are positive or negative integers. The energy of the electron in the state $\psi_{\mathbf{k}}$ is given by

$$E_{\mathbf{k}} = \hbar^2k^2/2m \tag{1.3}$$

where the zero of energy coincides with the bottom of the conduction band. For a complete description of an electron state we must also specify the spin orientation of the electron. For given **k** we have two states (spin up, spin down) with the same spatial wave function [given by Eq. (1.1)]. Having this in mind and letting L go to infinity we find that the number of electron states per unit volume with energy between E and $E + dE$ is given by

$$\rho(E)\,dE = \frac{2}{(2\pi)^3} \iint\int_{E}^{E+dE} d^3k \tag{1.4a}$$

$$= \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}\,dE \tag{1.4b}$$

The probability of an electron state with energy E being occupied (at equilibrium) is given by the Fermi–Dirac distribution function

$$f(E) = \frac{1}{1 + \exp\left[(E - E_F)/k_B T\right]} \tag{1.5}$$

where k_B is Boltzmann's constant, T is the absolute temperature, and E_F is the Fermi level. The latter is determined by the requirement

$$\int_0^\infty \rho(E) f(E)\,dE = N_c \tag{1.6}$$

where N_c is the number of conduction band electrons per unit volume and it is in effect an empirical parameter. For a metal, E_F is practically independent of temperature (see, e.g., Peierls, 1955) and can, in most cases, be replaced by its value at $T = 0$. The latter is given by

$$E_F = \frac{\hbar^2}{2m}(3\pi^2 N_c)^{2/3} \tag{1.7}$$

Apart from the above general formulas we shall, for the subsequent development of the theory of electron emission, require an expression for the number of electrons which, under equilibrium conditions, cross a unit area (we shall assume without any loss of generality that this is parallel to the xy plane) from left to right, per unit time, with total energy between E and $E + dE$ and normal energy, defined by

$$W = \frac{\hbar^2 k_z^2}{2m} \tag{1.8}$$

between W and $W + dW$. We denote this quantity by $N(E,W)\,dE\,dW$. We have

$$N(E,W)\,dE\,dW = \frac{2f(E)}{(2\pi)^3} \iiint\limits_{\{E,W\}} v_z d^3k \tag{1.9}$$

where

$$v_z \equiv \frac{1}{\hbar}\frac{\partial E_{\mathbf{k}}}{\partial k_z} = \frac{\hbar k_z}{m} \tag{1.10}$$

is the velocity of the electron normal to the unit area under consideration, and $\{E,W\}$ indicates that only states with total energy between E and $E + dE$ and normal energy between $W + dW$ corresponding to $v_z > 0$ are to be included in the integration.

One can easily show that

$$N(E,W)\,dE\,dW = \frac{m}{2\pi^2\hbar^3} f(E)\,dE\,dW \tag{1.11}$$

1.2. SCATTERING BY ONE-DIMENSIONAL BARRIERS

Consider a potential barrier $V(z)$ such as the one shown in Fig. 1.1. Let an electron with total energy E and wave vector $\mathbf{k}_{\parallel} = (k_x, k_y)$ be incident on this

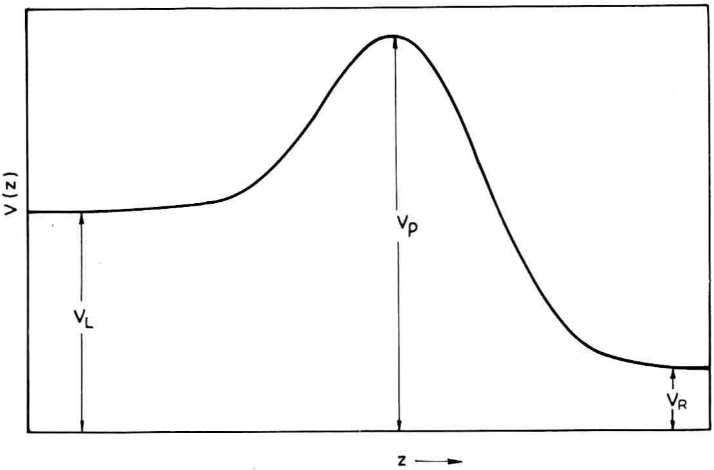

FIGURE 1.1

One-dimensional potential barrier.

barrier from the left. The electron will be partly reflected by the barrier and partly transmitted through it. We can calculate the reflection and transmission coefficients, as defined by Eqs. (1.17) and (1.18), as follows. Since the potential depends only on the z coordinate, the electronic wave function has the form

$$\psi = e^{i\mathbf{k}_{\|}\cdot\mathbf{r}_{\|}}u(z) \tag{1.12}$$

where $\mathbf{r}_{\|} \equiv (x,y)$ and $u(z)$ satisfies the following equation:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dz^2} + V(z)u = Wu(z) \tag{1.13}$$

where the normal energy $W = E - \hbar^2k_{\|}^2/2m > V_L$ and may lie above or below the top of the barrier, denoted by V_p in Fig. 1.1. In the region of constant potential ($V = V_R$) to the right of the barrier the wave function has the following form:

$$u(z) = C \exp(iq_Rz) \tag{1.14}$$

with

$$q_R = \left[\frac{2m}{\hbar^2}(W - V_R)\right]^{1/2}$$

which represents a transmitted wave propagating in the positive z direction. In the region of constant potential ($V = V_L$) to the left of the barrier the wave function has the form

$$u(z) = A \exp(iq_Lz) + B \exp(-iq_Lz) \tag{1.15}$$

with

$$q_L = \left[\frac{2m(W - V_L)}{\hbar^2}\right]^{1/2}$$

The first term in the above equation represents the incident wave and the second term represents the reflected wave. The incident, reflected, and transmitted current densities are calculated in the usual manner from the formula (see, e.g., Landau and Lifshitz, 1958)

$$j_{z,\alpha} = \frac{\hbar}{2mi}\left(f_\alpha^*\frac{\partial}{\partial z}f_\alpha - f_\alpha\frac{\partial}{\partial z}f_\alpha^*\right) \tag{1.16}$$

where f_α stands for the incident, reflected, and transmitted wave, respectively. The transmission coefficient is defined by

$$D(W) \equiv \frac{j_{z,\mathrm{tra}}}{j_{z,\mathrm{inc}}} = \frac{q_R}{q_L}\left|\frac{C}{A}\right|^2 \tag{1.17}$$

and the reflection coefficient by

$$R(W) \equiv \frac{j_{z,\mathrm{ref}}}{j_{z,\mathrm{inc}}} = \left|\frac{B}{A}\right|^2 \tag{1.18}$$

Explicit analytic expressions for D and R can be obtained only for a few specific potential barriers. On the other hand, one can obtain $D(W)$ and $R(W)$ numerically, and without much difficulty, for *any* barrier which depends only on the z coordinate. This can be done as follows. One starts from the known wave function [Eq. (1.14)] at some point to the right of the barrier where the potential is constant. The numerical value of C is unimportant and can be put equal to unity. One then proceeds to integrate numerically the Schrödinger equation, Eq. (1.13), moving from right to left in a step-by-step procedure using one of a number of methods which are available for this purpose (see, e.g., Buckingham, 1962). By carrying the integration into the region of constant potential to the left of the barrier, we obtain the wave function there and hence the values of A and B in Eq. (1.15), and hence $D(W)$ and $R(W)$. We note that when the potential barrier decreases slowly and monotonically to the right of the barrier top, one does not need to start the integration from the region of constant potential, which, thus, becomes irrelevant to the transmission problem. Under the above conditions there always exists a region, $z \geq z_r$, to the right of the barrier peak where the ordinary WKB approximation is valid (see, e.g., Landau and Lifshitz, 1958), and there the wave function appropriate to a transmitted wave has the form

$$u(z) = \frac{C}{[\lambda(z)]^{1/2}} \exp\left[i \int_{z_r}^{z} \lambda(z)\, dz\right] \tag{1.19}$$

where

$$\lambda(z) \equiv \left\{\frac{2m}{\hbar^2}[W - V(z)]\right\}^{1/2} \tag{1.20}$$

Obviously $W > V(z)$ for $z > z_r$. In this case the transmission coefficient is given by

$$D(W) = \frac{1}{q_L}\left|\frac{C}{A}\right|^2 \tag{1.21}$$

If we take advantage of Eq. (1.19) we can start the numerical integration at z_r. Again, the numerical value of C is unimportant and can be chosen arbitrarily.

Although the above procedure for calculating the transmission coefficient is easy to carry out and should be used when the situation demands an accurate analysis of specific experimental data, it is not appropriate for a general analysis of electron emission phenomena. For that purpose a less accurate method leading to an analytic expression for the transmission coefficient (at least for certain values of the physical parameters) is much preferable. Such a method, and one which has been extensively used in the study of electron emission, has been developed by Miller and Good (1953a). Their method is a generalization of the ordinary WKB method and it leads to the WKB results under certain limiting conditions. Their theory applies to the case of a slowly varying potential barrier, with only two classical turning points. This means that there are only two real roots of the equation

$$W - V(z) = 0 \tag{1.22}$$

when W lies below the top of the barrier. We denote them by z_1 and z_2 and we assume that $z_1 < z_2$. Also, it is assumed that when W goes above the top of the barrier, the two real roots of Eq. (1.22) go unambiguously into two complex roots, the one being the complex conjugate of the other since $V(z)$ is real. We denote by z_1 the one with the positive imaginary part, and by z_2 the one with the negative imaginary part. The method of Miller and Good is not applicable if $[W - V(z)]$ has additional zeros or singularities in the vicinity of z_1 or z_2. When the conditions for the applicability of their method are satisfied as, for example, in the case of the barrier shown in Fig. 1.1, the transmission coefficient is given to a good approximation by the following formula:

$$D(W) = \{1 + \exp[-A(W)]\}^{-1} \tag{1.23}$$

where

$$A(W) = 2i \int_{z_1}^{z_2} \lambda(\xi)\, d\xi \tag{1.24}$$

where $\lambda(\xi)$ is given by Eq. (1.20). The normal energy W may lie above or below the top of the barrier. In performing the ξ integration in Eq. (1.24) one must remember that z_1 and z_2 and hence ξ are complex when W lies above the top of the barrier. In performing the ξ integration that branch of $\lambda(\xi)$ is taken for which $-\pi < \arg[\lambda^2(\xi)] \leq \pi$. Accordingly, when ξ is real we get $\arg[\lambda(\xi)] = 0$ for $W > V(\xi)$ and $\arg[\lambda(\xi)] = \pi/2$ for $W < V(\xi)$. One can easily show that $A(W)$ is always real and that it is positive for energies above the top of the barrier and negative for energies below the top of the barrier. It is also obvious that when the energy W lies well below the barrier top, we have $\exp[-A(W)] \gg 1$ and Eq. (1.23) reduces to the well-known formula

$$D(W) \simeq \exp\left[-2\int_{z1}^{z2} |\lambda(z)|\, dz\right] \tag{1.25}$$

which is obtained by the ordinary WKB method (see, e.g., Landau and Lifshitz, 1958). We note that when the incident energy is equal to the barrier height we obtain $A = 0$ and the WKB formula, Eq. (1.25), gives $D = 1$, whereas the Miller and Good formula, Eq. (1.23), gives $D = 0.5$. A comparison with exact results made by Miller and Good (1953a) for a barrier similar to the one shown in Fig. 1.1 suggests that Eq. (1.23) underestimates the transmission coefficient by 10% or so in the energy region around the top of the barrier. The approximation improves considerably as we move away from the barrier top and is very accurate for energies sufficiently away from it. The accuracy at a given energy will, of course, depend on the shape of the barrier.

1.3. ELECTRON EMISSION FROM A METAL SURFACE

Consider a semi-infinite metal occupying the half-space from $z = -\infty$ to $z \simeq 0$. According to the free-electron theory of metals an electron inside the metal sees a constant (zero) potential. On the other hand, we know from experience that at zero temperature a certain minimum energy, equal to the work function ϕ, must be supplied to the metal before an electron can escape from it. We also know from classical electrostatics that an electron situated at a finite distance from the plane surface of a perfect conductor is attracted to it, by the well-known "image" force: $-e^2/4z^2$. (The minus sign arises because we have assumed that the z axis points outwards from the metal.) Hence, the potential energy of the electron on the vacuum side of the metal–vacuum interface is asymptotically given by

$$V(z) \simeq E_F + \phi - e^2/4z \tag{1.26}$$

In recent years, a lot of effort has been put into microscopic studies of the potential barrier at a metal–vacuum interface (see, e.g., Lang, 1973; Inkson, 1971; Appelbaum and Hamann, 1972a; Harris and Jones, 1973; 1974). All investigators agree that Eq. (1.26) is valid for $z >$ (3 Å or so). The detailed shape of the barrier for $z <$ 3 Å depends on the metal surface under consideration. In the traditional (free-electron) theories of electron emission it is assumed that Eq. (1.26) remains valid right up to a point z_c such that $V(z_c) = 0$. When an external electric field F is applied to the surface, a term $-eFz$ is added on the right of Eq. (1.26). In electron emission experiments $F > 0$. In summary, the potential energy field seen by an electron in an electron emission experiment is approximated by

$$\begin{aligned} V(z) &= E_F + \phi - \frac{e^2}{4z} - eFz \qquad \text{for } z > z_c \\ &= 0 \qquad \text{for } z < z_c \end{aligned} \tag{1.27}$$

where z_c is determined by $V(z_c) = 0$. In Fig. 1.2 we show this potential barrier for a typical value of $E_F + \phi$ and for a value of the applied field appropriate to a field emission experiment. We note that the peak of the barrier described by Eq. (1.27) occurs at

$$\begin{aligned} z_m &= (e/4F)^{1/2} \\ &= 1.9/F^{1/2}\ \text{Å} \qquad (\text{with } F \text{ in V/Å}) \end{aligned} \tag{1.28}$$

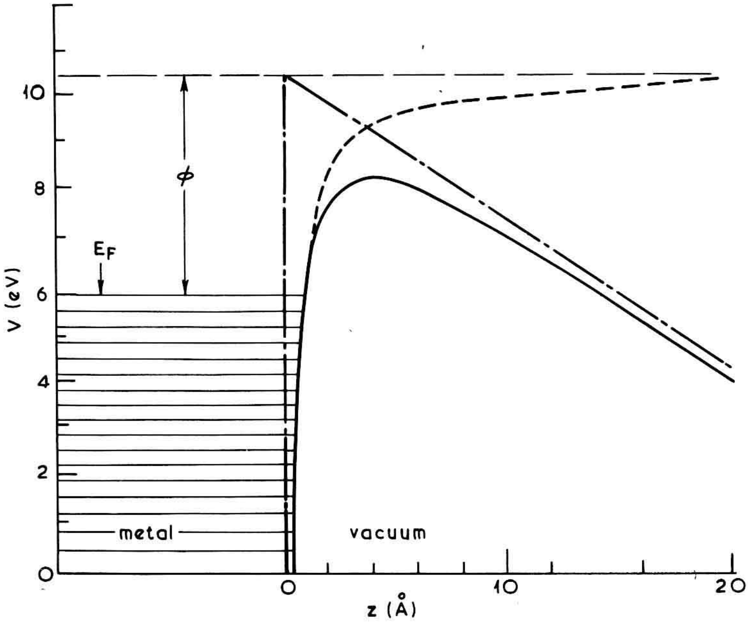

FIGURE 1.2

The surface potential barrier seen by an electron in a field emission experiment (solid line). The contributions of the image potential and of the applied field ($F = 0.3$ V/Å) are shown by the broken and the broken-solid line, respectively.

and has the value

$$\begin{aligned} V_{\max} &= E_F + \phi - (e^3F)^{1/2} \\ &= E_F + \phi - 3.79F^{1/2}\,\text{eV} \qquad (\text{with } F \text{ in V/Å}) \end{aligned} \tag{1.29}$$

In order to construct a theory of electron emission from metal surfaces we proceed as follows. We assume (this is justified because the electric field is negligible inside the metal) that the number of electrons with normal energy between W and $W + dW$ impinging on the surface barrier from within the metal when a current is emitted is practically identical with its equilibrium value given by

$$\begin{aligned} N(W,T)\,dW &= \frac{m\,dW}{2\pi^2\hbar^3}\int_W^\infty f(E)\,dE \\ &= \frac{mk_BT}{2\pi^2\hbar^3}\ln\left[1 + \exp\left(-\frac{W - E_F}{k_BT}\right)\right] dW \end{aligned} \tag{1.30}$$

Each of these electrons has a probability $D(W)$ to be transmitted through the surface potential barrier. Hence, the emitted current density, i.e., the number of electrons emitted per unit area per unit time multiplied by the magnitude of the electronic charge, is given by

$$J(F,T) = e\int_0^\infty N(W,T)D(W)\,dW \tag{1.31}$$

where T and F denote as usual the temperature and the applied field, respectively. Murphy and Good (1956) have shown that if one assumes the validity of the surface barrier given by Eq. (1.27) and if one uses Eq. (1.23) for the calculation of the transmission coefficient for this barrier, one obtains, starting from Eq. (1.31), an expression for $J(F,T)$ valid for any values of F and T, which in turn, leads to explicit and relatively simple formulas for $J(F,T)$ for certain regions of F and T. As we shall see, the Murphy and Good theory leads in a systematic way to the Fowler–Nordheim formula for field emission, i.e., emission at very low temperatures with a strong applied field, and to the Richardson and Schottky formulas for thermionic emission, i.e., emission at high temperatures with a weak or zero applied field.

The transmission coefficient for the potential barrier of Eq. (1.27) is, according to Eqs. (1.23) and (1.24), given by

$$D(W,F) = \{1 + \exp[Q(W)]\}^{-1} \tag{1.32}$$